5 CLAIMS

1. A process for applying a multilayer protective coating to a substrate having an electrically conductive surface, comprising:

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a first method of forming a silicate layer upon said electrically conductive surface, said first method comprising contacting at least a portion of said surface with a first medium comprising at least one silicate and having a basic pH and wherein said first medium is substantially free of chromates, to form a silicate layer, and

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a second method of electrolytically applying a synthetic resin layer upon the surface of said silicate layer, said second method comprising contacting at least a portion of said surface of said silicate layer with a second medium comprising a resinous ingredient, applying an electric current to said second medium wherein said surface is employed as an electrode, to form a synthetic resin layer.

- 2. The process of claim 1, wherein said substrate is a metal substrate.
- 3. The process of claim 1 or 2, wherein said substrate is a metal substrate made of a material selected from the group consisting of steel, zinc or zinc/nickel coated steel, aluminum, zinc or zinc/nickel coated aluminum, iron, zinc or zinc/nickel coated iron, nickel, copper, zinc, magnesium, and alloys thereof.
- 4. The process of any one of claims 1 to 3, wherein said first method further comprises introducing an electric current to said first medium wherein said surface is employed as a cathode.

- 5. The process of any one of claims 1 to 4, wherein said first medium is an aqueous medium.
- 6. The process of any one of claims 1 to 5, wherein the pH of said first medium is adjusted to a value of about 10 to about 11.5.
 - 7. The process of any one of claims 1 to 6, wherein said first medium contains sodium silicate.
- 10 8. The process of any one of claims 1 to 7, wherein said first medium contains silicate in a concentration of about 1 to about 25 wt.%, in particular about 5 to 15 wt.%.
- 9. The process of any one of claims 1 to 8, wherein in said first method said silicate layer is applied at a thickness of about 100 to about 2500 Angstroms.
 - 10. The process of any one of claims 1 to 9, wherein said first method further comprises:

rinsing the surface; and drying the surface.

- 11. The process of any one of claims 1 to 10, wherein said second medium is an aqueous medium.
- 12. The process of any one of claims 1 to 11, wherein said resinous ingredient in said second method comprises a resin selected from the group consisting of cathodically applied electrocoating epoxy resins, anodically applied electrocoating epoxy resins, cathodically applied electrocoating acrylic resins, and anodically applied electrocoating acrylic resins.

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- 13. The process of any one of claims 1 to 12, wherein said resinous ingredient in said second medium comprises a cationic resin and a crosslinking agent.
- 14. The process of any one of claims 1 to 13, wherein said resinous ingredient in said second medium comprises a cathodically applied blocked isocyanate epoxy resin.
 - 15. The process of any one of claims 1 to 14, wherein the pH of said second medium is adjusted to a value of from about 4.5 to about 6.5.
- 16. The process of any one of claims 1 to 15, wherein said surface in said second method is employed as cathode.

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- 17. The process of any one of claims 1 to 16, wherein said second medium contains said ionic resinous ingredient in a concentration of about 1 to about 25 wt.%, in particular about 5 to about 15 wt.%.
- 18. The process of any one of claims 1 to 17, wherein in said second method said synthetic resin layer is applied at a thickness of about 5 to about 25 microns, in particular about 8 to about 15 microns.

19. The process of any one of claims 1 to 18, wherein said second method further comprises drying said synthetic resin layer.

- 20. The process of any one of claims 1 to 19, wherein said second method further comprises drying said synthetic resin layer at a temperature of about 180 to about 250 °C.
 - 21. A corrosion resistant article comprising a metal body and a substantially chromate free protective coating applied on at least one surface of said metal body, said protective coating comprising

a silicate layer comprising at least one silicate; and

a synthetic resin layer comprising at least one electrolytically applied synthetic resin.

- The article of claim 21, wherein said metal body is made from a metal
 selected from the group consisting of steel, stainless steel, aluminum, iron, nickel, copper, zinc, magnesium, and alloys thereof.
 - 23. The article of claim 21 or 22, wherein said silicate layer comprises electrolytically applied silicate.

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- 24. The article of any one of claims 21 to 23, wherein said silicate layer contains an alkali silicate.
- 25. The article of any one of claims 21 to 24, wherein said silicate layer comprises a disilicate mineral structure.
 - 26. The article of any one of claims 21 to 25, wherein said silicate layer has a thickness of about 100 to about 2500 Angstroms.
- 27. The article of any one of claims 21 to 26, wherein said synthetic resin layer comprises a resin selected from the group consisting of cathodically applied electrocoating epoxy resins, anodically applied electrocoating epoxy resins, cathodically applied electrocoating acrylic resins.
- 25 28. The article of any one of claims 21 to 27, wherein said synthetic resin layer comprises a cathodically applied blocked isocyanate epoxy resin.
 - 29. The article of any one of claims 21 to 28, wherein the synthetic resin layer has a thickness of about 5 to about 25 microns.
 - 30. The article of any one of claims 21 to 29, wherein said protective coating

further comprises a zinc layer comprising zinc, said zinc layer being interposed between the surface of said metal body and said silicate layer.

- 31. The article of claim 30, wherein said zinc layer is applied between said metal body and said silicate layer.
 - 32. The article of claim 30, wherein said zinc layer comprises electrolytically applied zinc.
- 10 33. The article of claim 30, wherein said zinc layer has a thickness of about 1 to about 75 microns.
 - 34. The article of any one of claims 21 to 33, wherein said protective coating is substantially phosphate free

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35. The article of any one of claims 21 to 34, wherein said protective coating comprises zinc and said article has an ASTM B117 exposure to white rust of greater than 200 hours.